Salt Concentration Dependence of Counterion Condensation in Sodium Polystyrene Sulfonate Brush(Poster session 2, New Frontiers in Colloidal Physics : A Bridge between Micro- and Macroscopic Concepts in Soft Matter)

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Salt Concentration Dependence of Counterion Condensation in Sodium Polystyrene Sulfonate Brush

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高分子電解質ブラシは、高分子の２次元的束縛とクーロン相互作用の競合などが基礎科学的に興味を持たれているのみならず、その生体親和性の高さやイオン相互作用の観点から新しいコーティング技術としても期待されている[1]。しかしこの分野は、理論的研究は先行しているものの実験的には未だ発展途上である。特に対イオン分布については、X線小角散乱や中性子反射率を用いた報告など数例があるのみで、外部環境に対する依存性やブラシ層への凝集量など詳細な挙動は明らかになっていない[2]。

そこで我々はζ電位測定を採用し、高分子電解質ブラシ層における帯電密度を通して対イオン凝集状態を調べた。サンプルは高電荷密度高分子電解質ブラシとしてポリスチレンスルホン酸ナトリウムを採用し、アニオン重合によって分子量分散を低く抑えた高分子鎖をシリコン基板上に結合したものを用いた[3]。測定されたζ電位値はPoisson-Boltzmann方程式によって解析され、対イオンのブラシ層内への凝集量を求めることにより、非凝集イオン量が水中の添加塩濃度に対して指数関数的に増加することを見いだした。

Polyelectrolyte brush is gathering considerable interests from both scientific and engineering viewpoints: protein immobilization on the brushes with their secondary structure nearly undisturbed has been found in recent years, for example[1]. Experimental researches for this system, however, are scarce other than theoretical and simulation ones because of substantial difficulty in the sample preparation. Counterion condensation is one of the most primitive and important topics about the system, which is also involved in adsorption of charged molecules like proteins. Proteins adsorb and desorb on polyelectrolyte brushes in low and high ionic strength conditions, respectively. Though the distribution profile of counterions has been investigated using X-ray or neutron, its detailed dependency on parameters and their condensed or immobilized amount still remain unexplored[2].

Then we investigated the counterion condensation in a planar strong polyelectrolyte, sodium polystyrene sulfonate (NaPSS), brush under a variety of salt, sodium chloride (NaCl), concentration conditions. Zeta potential measurements were performed, which differentiates ions with fluidity in bulk water from that immobilized in

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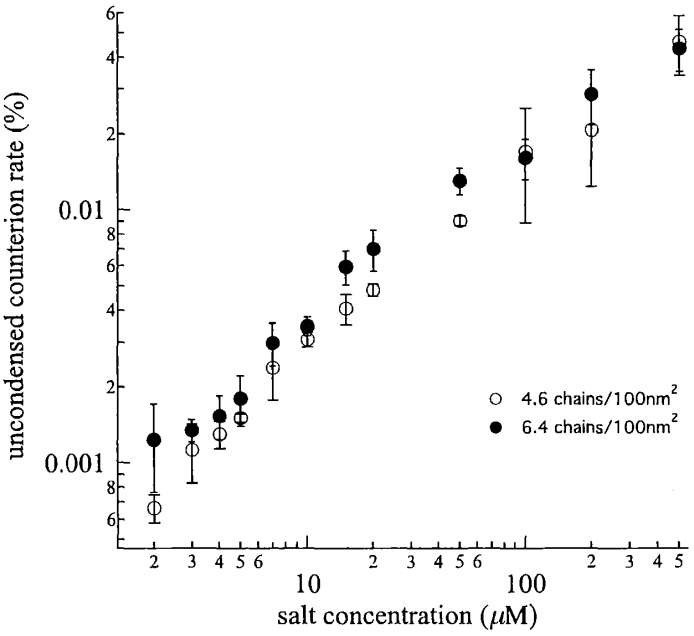

Figure 1. Salt concentration dependence of the uncondensed counterion rate on sodium polystyrene sulfonate brush with different graft density.

the brush layer due to its measurement principle.

The brushes were prepared by "grafting-to" method[3]: $SiCl_3$-terminated polystyrene with mono-disperse molecular weight was synthesized by anion polymerization and grafted to silicon substrate then sulfonated. Graft density and sulfonation rate were defined by ellipsometry and FT-IR measurements, respectively.

The results were analyzed with Poisson-Boltzmann equation to obtain the surface charge density that is directly connected to uncondensed counterions by electroneutrality condition. Its added salt concentration dependence has revealed the counterion immobilization to be weakened by the salt addition. Figure 1 shows the salt concentration dependence of the uncondensed counterion rate that exhibits a power law with its index of 0.7.

References

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